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ECBC-TR-535

DEGRADATION OF THE BLISTER AGENT BIS(2-CHLOROETHYL) SULFIDE AND SIMULANT 2-CHLOROETHYL PHENYL SULFIDE ON CONCRETE

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April 2007

20070508022

ABERDEEN PROVING GROUND, MD 21010-5424

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REPORT DOCUMENTATION PAGE		*Form Approved* *OMB No. 0704-0188*

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1. REPORT DATE *(DD-MM-YYYY)* XX-04-2007	2. REPORT TYPE Final	3. DATES COVERED *(From - To)* Jun 2003 - Dec 2006

4. TITLE AND SUBTITLE

Degradation of the Blister Agent Bis(2-chloroethyl) Sulfide and Simulant 2-Chloroethyl Phenyl Sulfide on Concrete

5a. CONTRACT NUMBER
DAAD13-03-D-0017

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

Brevett, Carol A.S.; Nickol, Robert G. (SAIC); Sumpter, Kenneth B.; and Wagner, George W. (ECBC)

5d. PROJECT NUMBER
206023.84BPO

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
DIR. ECBC. ATTN: AMSRD-ECB-RT-PD. APG. MD 21010-5424

SAIC, 3465A Box Hill Corporate Drive, Abingdon, MD 21009

8. PERFORMING ORGANIZATION REPORT NUMBER
ECBC-TR-535

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT
The degradation of the Chemical Warfare Agent sulfur mustard, bis(2-chloroethyl) sulfide, and the half-mustard simulant, 2-chloroethyl phenyl sulfide was studied on ambient and moist concrete using ^{13}C solid-state magic-angle-spinning nuclear magnetic resonance (SSMAS NMR). Two samples of concrete made by the same formulation, but differing in age and surface alkalinity, were used. The 2-chloroethyl phenyl sulfide hydrolyzed to form the 2-hydroxyethyl phenyl sulfide, which then formed the ether on all of the concrete samples. The sulfur mustard formed minor amounts of vinyl species on the newer, more alkaline concrete samples. The sulfur mustard eventually degraded to thiodiglycol and 1,4-oxathiane via the intermediate sulfonium ions H-2TG and $O(CH_2CH_2)_2S^+CH_2CH_2OH$ on all of the concrete samples.

15. SUBJECT TERMS

Mustard	Bis(2-chloroethyl) Sulfide	CEPS	HD
Concrete agent fate	Sulfonium ion	Degradation	H

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Sandra J. Johnson
a. REPORT U	b. ABSTRACT U	c. THIS PAGE U	UL	29	19b. TELEPHONE NUMBER *(include area code)* (410) 436-2914

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. Z39.18

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# DEGRADATION OF THE BLISTER AGENT BIS(2-CHLOROETHYL) SULFIDE AND SIMULANT 2-CHLOROETHYL PHENYL SULFIDE ON CONCRETE

1.   INTRODUCTION

The Chemical Warfare Agent (CWA) sulfur mustard [bis(2-chloroethyl) sulfide, $(ClCH_2CH_2)_2S$, commonly abbreviated H for munitions grade and HD for distilled] was used during World Wars I and II[1] and was used recently in the Iran-Iraq wars of the 1980s.[2] Poor disposal methods of unused sulfur mustard stockpiles and ordnance, especially ocean dumping, have led to the resurfacing and continuance of sulfur mustard in the environment.[3,4] In addition, there is the possibility that various terrorist groups will manufacture CWAs and use them to harm civilian populations, as happened when the group Aum Shinrikyo released Sarin (GB) in the Tokyo subway in March 1995.[5]

In the event of contamination of a large area with sulfur mustard, decisions must be made whether to decontaminate an area or allow resumption of normal operations after an acceptable waiting period. Knowledge of whether the CWA will degrade on a given surface, the correct assessment of the identity, and amount and toxicity of products formed is crucial for making correct decisions about the need for decontamination. The reactivity of sulfur mustard with a variety of decontamination solutions and powders has been elucidated.[6]

Environmentally, sulfur mustard has been observed to persist for 4 years in soil.[7] Wagner and MacIver[8] used ^{13}C SSMAS NMR to show that sulfur mustard persisted for several weeks on dry soil but hydrolyzed and oligomerized to form the toxic sulfonium ions CH-TG and H-2TG within 2 days when water was added. The half-mustard simulant, 2-chloroethyl phenyl sulfide (CEPS), did not react on dry soil but with the addition of water, hydrolyzed to form the alcohol, 2-hydroxyethyl phenyl sulfide, HEPS, and the ether $(PhSCH_2CH_2OCH_2CH_2SPh)$. CEPS and sulfur mustard initially gave narrow peaks; these became broader with time, indicating surface-sorption on the soil particles. The addition of water to the sulfur mustard on soil yielded narrower peaks, thus indicating that the water had sorbed onto the soil and thus displaced the sulfur mustard from the soil surface.

Yang[9] et al. showed that although sulfur mustard has low solubility in water (1 mg/mL), forming droplets within it, reactions occurred at the water-sulfur mustard interface to form the hydrolysis products chlorohydrin (CH, $ClCH_2CH_2SCH_2CH_2OH$) and thiodiglycol (TDG, $HOCH_2CH_2SCH_2CH_2OH$), which subsequently formed the sulfonium ions H-2TG and CH-TG (Scheme 1).[10, 11] Furthermore, the sulfonium ions formed had the potential to reform mustard in the presence of chloride ions. Tilley[12] measured the hydrolysis of 0.35 mM sulfur mustard in aqueous mixtures of ethanol, acetone, and dimethyl sulfoxide at 25 °C, and calculated a hydrolysis half-life for mustard in pure water of 4 min. Bartlett and Swain,[13] recognizing that the hydrolysis of mustard to thiodiglycol was a two-step process, first measured the hydrolysis of the intermediate, chlorohydrin, in 5% acetone at 25 °C and then measured the hydrolysis of HD under the same conditions. This yielded a sulfur mustard hydrolysis half-life of 4.3 min. The half-life of 2 mM sulfur mustard in D_2O at 22 °C as measured by Logan[14] was 7 min; thus showing a kinetic isotope effect of ~2.
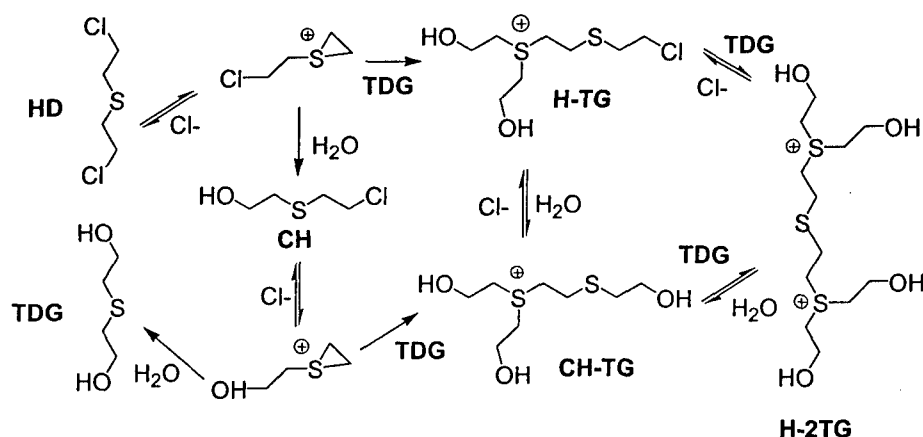
Scheme 1. Formation of H-2TG from sulfur mustard[10, 11]

Brevett et al. showed that sulfur mustard on wet sand degraded to form TDG, H-2TG and CH-TG.[15] Brevett et al. also showed that sulfur mustard on ambient concrete would remain as mustard for 12 weeks, but after the passage of two weeks, it was non-extractable.[16]

Tang et al.[17] showed that sulfur mustard vapor diffused into cement, and droplets of sulfur mustard migrated through a layer of cement at the rate of 1.3×10^{-4} cm/min. Loss of mustard and formation of products were detected by extraction with acetonitrile followed by gas chromatography/mass spectrometry (GC/MS). The rate for mustard loss was calculated to be 4.8×10^{-5} min^{-1}, which corresponded to a first-order half-life of 10 days. Products observed in the GC/MS were 2-chloroethyl vinyl sulfide (CEVS), 1,4-oxathiane, Q (sesquimustard, $ClCH_2CH_2SCH_2CH_2SCH_2CH_2Cl$), and mustard disulfide ($(ClCH_2CH_2S)_2$).

When sulfur mustard was placed on MgO[18] or CaO,[19] the products TDG, CEVS, and divinyl sulfide (DVS) were detected using ^{13}C SSMAS NMR. Degradation of sulfur mustard on CaO also led to minor amounts of sulfonium ions. On the surface of ambient alumina, sulfur mustard reacted to give mostly TDG with minor amounts of CEVS and DVS. When excess water was added, the sulfonium ions H-2TG and CH-TG were formed, and $Al(H_2O)_6^{3+}$ was liberated from the surface.[20]

Karwacki et al.[21] showed that sulfur mustard degradation on dry coconut shell carbon (CSC) at 50 °C produced the elimination product, CEVS, and the cyclic ether 1,4-oxathiane. Wagner et al.[22] demonstrated that on wet CSC at 30 °C the products CH and TDG were produced in addition to the products that were formed on the dry CSC. The first-order half-life was 25 days. CEPS* was shown to migrate into the micropores and mesopores of activated charcoal, and the addition of oxidants to the charcoal resulted in the oxidation of the CEPS*. Prasad et al.[23] impregnated high surface area carbon with a variety of oxidizing agents to form the products CH, TDG, 1,4-oxathiane, 1,4-thiazane, and divinyl sulfone, depending upon the oxidant used.[24] Sharma et al. showed that carbon impregnated with a vanadium/ruthenium mixture would oxidize sulfur mustard to the sulfoxide.[25]

Wagner and Bartram[26] showed that CEPS on NaY zeolite hydrolyzed to HEPS, and HD formed the sulfonium ion H-2TG, whereas on AgY zeolite the CEPS formed the ether, and the HD formed 1,4-oxathiane and DVS.

In the current study, ^{13}C SSMAS NMR techniques were employed to study the degradation of sulfur mustard and the simulant CEPS on ambient and moist concrete, an environmentally relevant substrate that has not previously been studied in this manner.

2. EXPERIMENTAL PROCEDURES

2.1 Concrete and Mortar Substrates.

The C03 concrete sample was supplied by the U.S. Army Engineering Research and Development Center (Vicksburg, MS). The C90 concrete sample was supplied by the U.S. Air Force Civil Engineering Support Agency (Tyndall AFB, FL). These two samples had the same nominal formulation: 16.5% Portland cement, 34.2% natural river siliceous sand as fine aggregate, 49.3% Caldera Alabama limestone coarse aggregate, and a 0.45 water-to-cement ratio. One sample (named C03) was approximately 1 year old when used. The other sample (named C90) had been cored from a used runway and was estimated to be 10 to 20 years old. Monoliths of the year-old sample (C03) had a surface area of 1.3 m^2/g,[27] and the pH of 1 g concrete in 5 mL water, measured after 24 hr using pH paper, was 9. When ground, the year-old sample had a surface area of 2.0 m^2/g, and the pH of 0.1 g in 2 mL water, measured after 1 and 24 hr was 12. Monoliths of the aged sample (C90) had a surface area of 1.4 m^2/g, and the pH of 1 g concrete in 5 mL water, measured after 24 hr, was 7.5. When ground, the aged sample had a surface area of 1.9 m^2/g, and the pH values of 0.1 g concrete in 2 mL water, measured after 1 and 24 hr, were 8 and 8.5, respectively. These pH values did not change during the duration of the experiments.

All samples were thoroughly ground and sieved through a ~ 2 mm sieve before use, to ensure good spinning in the NMR rotor, which held 200 mg concrete.

2.2 Reagents.

The sulfur mustard, made locally, was 50% [13]C labeled at each carbon position, such that two ^{13}C would not be adjacent, and was 99.5% pure by GC. This allowed for good detection of the ^{13}C signal, but avoided the [13]C-^{13}C couplings that would be present if 100% labeling were used. The notation for the sulfur mustard used is HD*; H for sulfur mustard, D denoting that it had been distilled, and thus does not contain the impurities Q [sesquimustard, bis(2-chloroethylthio) ethane, $ClCH_2CH_2SCH_2CH_2SCH_2CH_2Cl$, 10 %], the cyclic ether 1,4-oxathiane, [$O(CH_2CH_2)_2S$, 3%) and 1,2-dichloroethane (3%)] , which are commonly present in munitions grade sulfur mustard and the * denoting ^{13}C-labeling. The ^{13}C chemical shifts for sulfur mustard on concrete were 44.5 ppm for $ClCH_2$ and 35.2 ppm for the CH_2S. Caution: sulfur mustard, bis(2-chloroethyl) sulfide is a potent vesicant, and care must be taken to prevent exposure to liquid or vapor. It should only be manipulated by trained personnel employing appropriate engineering controls and personal protective equipment.

The 2-chloroethyl phenyl sulfide, made locally, was 50% labeled on the ethyl moiety (hence, CEPS*); chemical shifts on concrete were 43.1 ppm for $ClCH_2$ and 36.4 ppm for

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the CH_2S. Thiodiglycol and 2-chloroethanol were obtained from Sigma-Aldrich Corporation, (Milwaukee, WI).

2.3   <u>NMR Instrumentation</u>.

The ^{13}C SSMAS NMR spectra for the HD* samples were collected at 9.4 Tesla using a Varian Inova NMR spectrometer equipped with a Doty Scientific 7 mm standard series VT-MAS (variable temperature magic angle spinning) probe using direct polarization, spinning rates of ~2000 Hz, and a 90° pulse width of 7.5 μsec.

The spectra for the CEPS* samples were collected at 9.4 Tesla using a Varian Inova NMR spectrometer equipped with a Doty Scientific 7 mm supersonic VT-MAS probe using direct polarization, spinning rates of ~3500 Hz, and a 90° pulse width of 4.5 μsec.

Delay times between pulses were at least 5 times the measured T_1, and spectra were referenced to external tetramethylsilane. Whenever the spinning side bands were so numerous that it was difficult to distinguish them from the product peaks, the spectra were acquired at two spin speeds. The apparent chemical shifts of the spinning side bands changed, but that of the products and reactants remained unchanged.

The rotors were packed with 200 mg ground concrete and 3 to 8 μL agent or simulant was added to the concrete using a microliter syringe. Doty Scientific double O-ring Kel-F caps on silicon nitride rotors were used. Distilled water, if used, was added second; a 15-fold molar excess was employed.

3.   RESULTS

3.1   <u>Ambient Aged Concrete</u>.

The initial spectrum of the CEPS* on the ambient aged concrete (C90) showed the presence of multiple spinning side bands (~ 25% of the total integrated peak area was in the spinning side bands). After 11 months, there was evidence that 20% of the CEPS* had reacted, as shown by peaks at 60.9 and 33.6 ppm, corresponding to HEPS; the spinning side bands were still present (Figure 1).

The HD* on the C90 concrete also initially gave ~28% of the total integrated peak area as spinning side bands. After 10 months, the peaks had broadened from 85 to 400 Hz, they appeared split, and the total integrated peak area had decreased to one-third of the original (Figure 2). The peak broadening and decrease in peak area were suggestive of the HD* absorbing onto the surface.

The 10-month sample of sulfur mustard was further examined by acquiring the spectrum with a recycle time of 0.3 sec rather than 10 sec. The products had a shorter T_1 relaxation time than the sulfur mustard (0.5 sec versus 2.0 sec, respectively), and thus, the spectra acquired with a shorter recycle time enhanced the product spectrum over that of the sulfur mustard (Figure 3). Thus, the split peaks were consistent with the presence of sulfur

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acquired with a shorter recycle time enhanced the product spectrum over that of the sulfur mustard (Figure 3). Thus, the split peaks were consistent with the presence of sulfur mustard and the products $O(CH_2CH_2)_2S^+CH_2CH_2OH$ (66, 57, 43, 32 ppm) and traces of 1,4-oxathiane (71, 27) ppm.
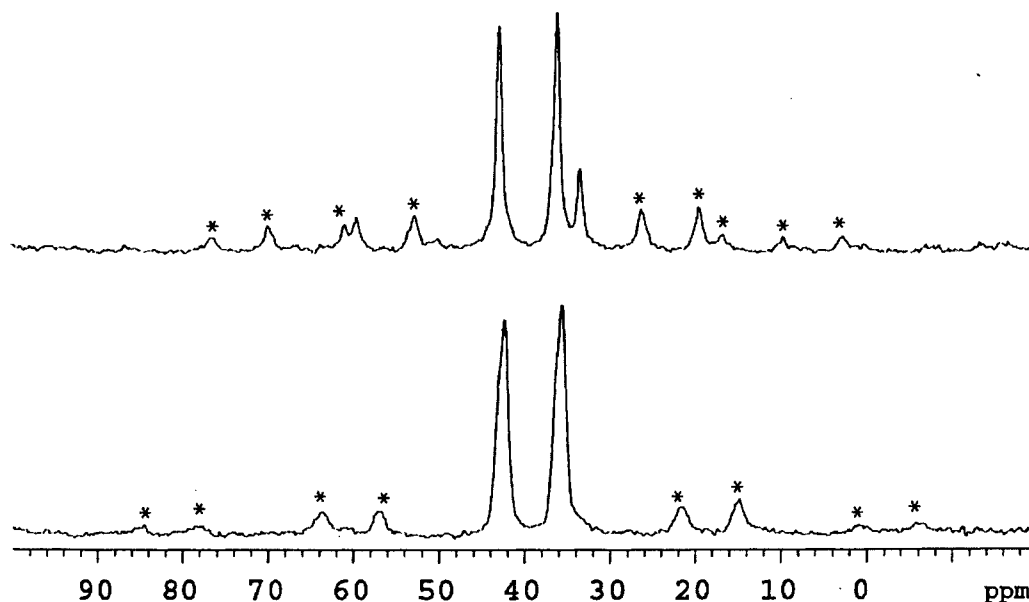

Figure 1. ^{13}C SSMAS NMR spectra of CEPS* on ambient C90 concrete: initial spectrum on bottom, 11-month spectrum on top. The * in the spectra designate the spinning side bands.
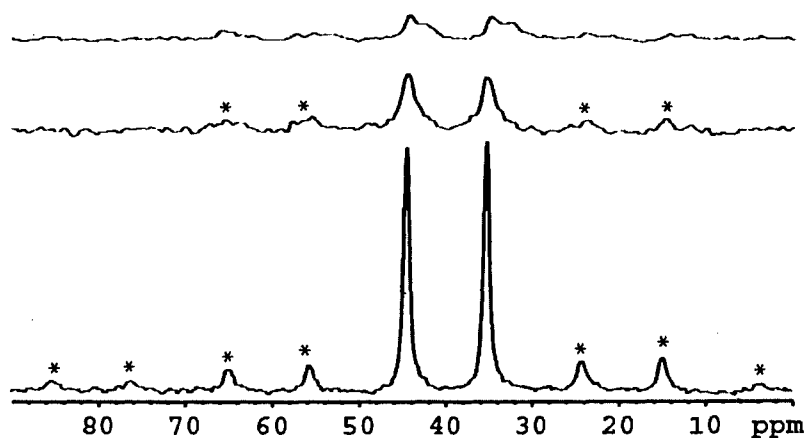

Figure 2. ^{13}C SSMAS NMR spectra of HD* on ambient C90 concrete; spectra in order from bottom to top were acquired at 1 hr, 14, and 39 weeks. The * in the spectra designate the spinning side bands.
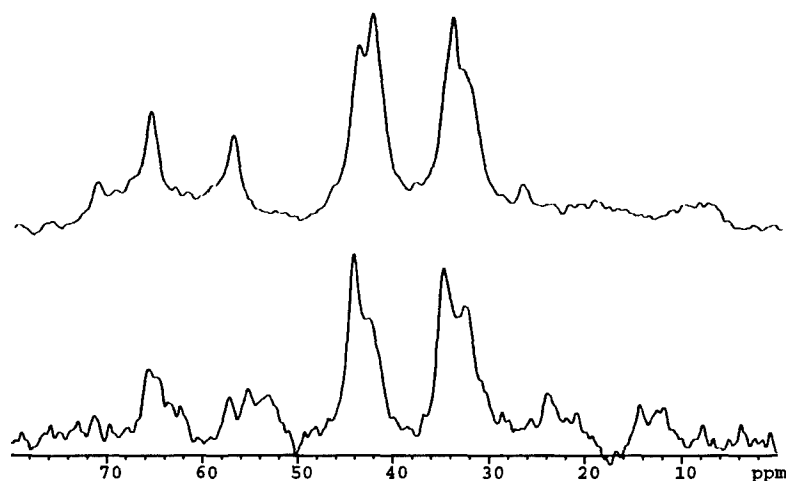
Figure 3. ^{13}C SSMAS NMR spectra of HD* on ambient C90 concrete at 39 weeks. The recycle times were 15 sec for the bottom spectrum and 0.3 sec for the top spectrum.

3.2 Ambient Year-old Concrete.

CEPS on the year-old concrete (C03) gradually decomposed to form the alcohol (61, 36 ppm) and the ether (70, 33 ppm) (Figure 4) with a first-order half-life of 19 weeks (Figure 5). There was an additional peak present at 63 ppm. The 61 and 63 ppm peaks were ~500 Hz wide, compared to ~80 Hz for the ether peaks and the CH_2S peak. This may indicate that the alcohol moiety was interacting with the surface of the concrete; the chemical shift of the carbon next to the sulfur would thus be unchanged. Only 8% of the total integrated peak area was observed in the spinning side bands.

When HD* was placed on concrete C03, the formation of hydroxyl (~62 ppm) and ether (~72 ppm) functionalities was observed at 1 week. By the end of 24 weeks ,(Figure 6) all of the mustard had disappeared, with a first-order half-life of 600 hr (Figure 7). Vinyl species at 112 and 130 ppm and a species at ~65 ppm were also observed. The ~65 ppm chemical shift was assigned to the sulfonium ion $O(CH_2CH_2)_2S^+CH_2CH_2OH$ (66, 57, 42 and 33 ppm),[28] which further degraded to 1,4-oxathiane (72 and 32 ppm), which accumulated, and 2-chloroethanol (63 and 46 ppm), which was not unequivocally observed. The aliphatic resonances of the vinyl compounds were hidden under those of the other products. The first-order half-life for the sulfonium ion loss was calculated to be 111 days. Only 5% of the total integrated peak area was observed in the spinning side bands.
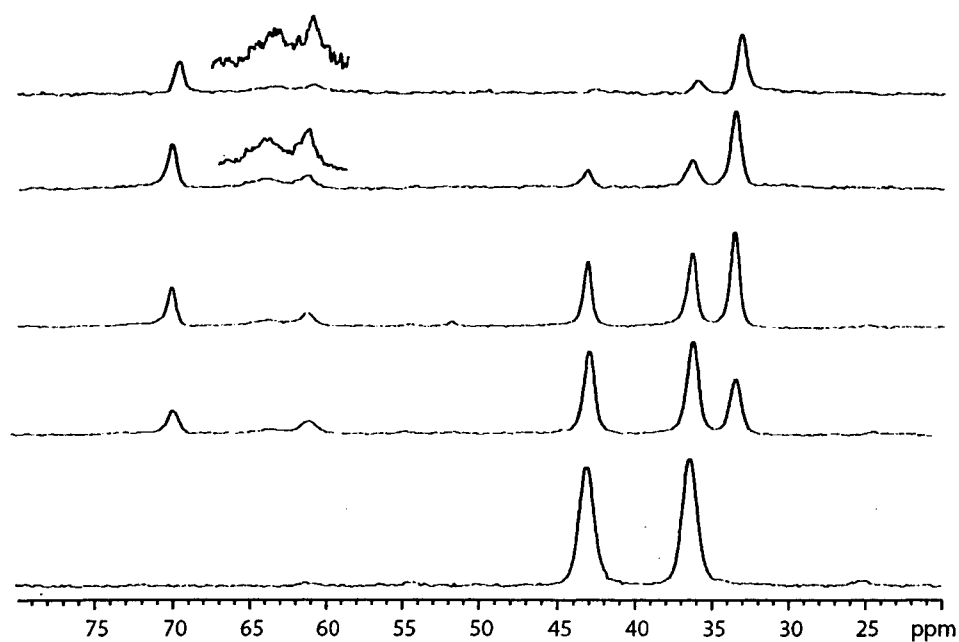
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Figure 4. ^{13}C SSMAS NMR spectra of CEPS* on C03 ambient concrete; spectra in order from bottom to top were acquired at 1 hr, 11, 22, 43, and 55 weeks.
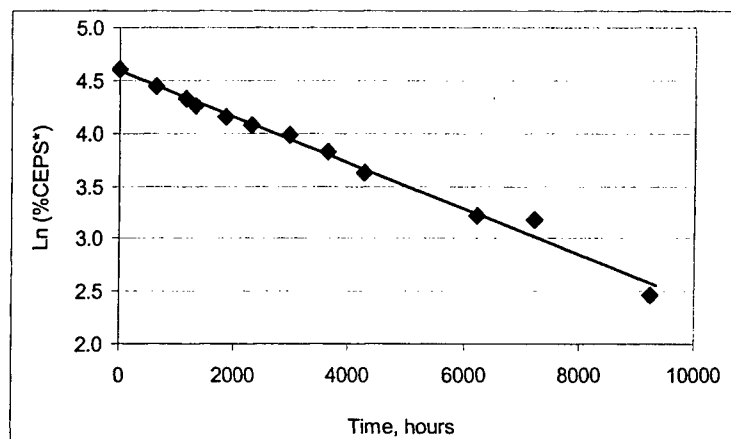
Figure 5. First-order kinetic plot for CEPS* on C03 ambient concrete; the calculated half-life was 19 weeks.

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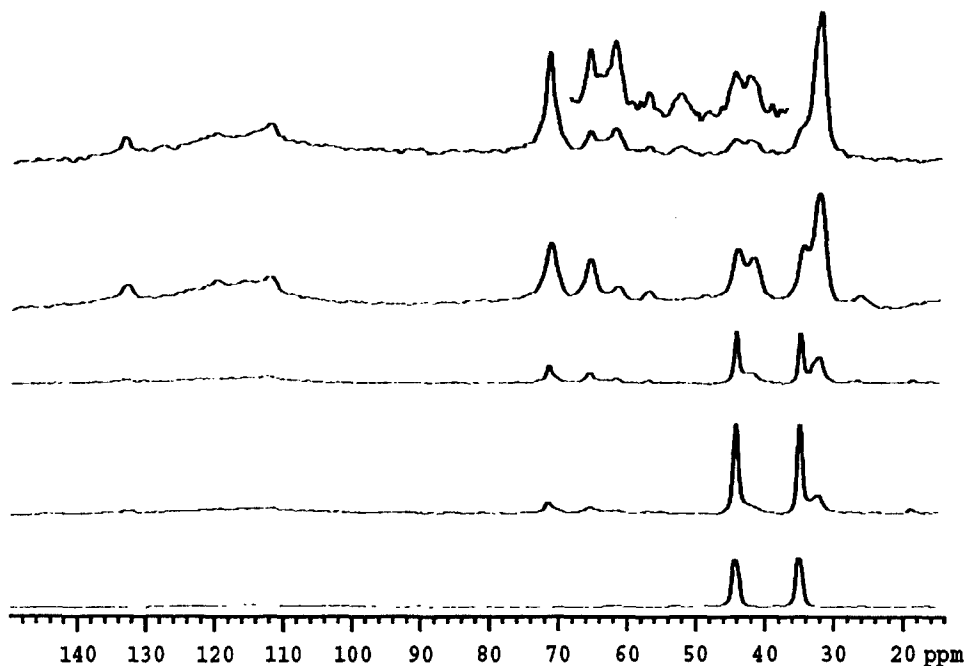
Figure 6. ^{13}C SSMAS NMR spectra of HD* on ambient concrete C03; spectra in order from bottom to top were acquired at 1 hr, 1 week; 5 weeks (3-fold magnification); 8, 10, and 24 weeks (12-fold magnification).
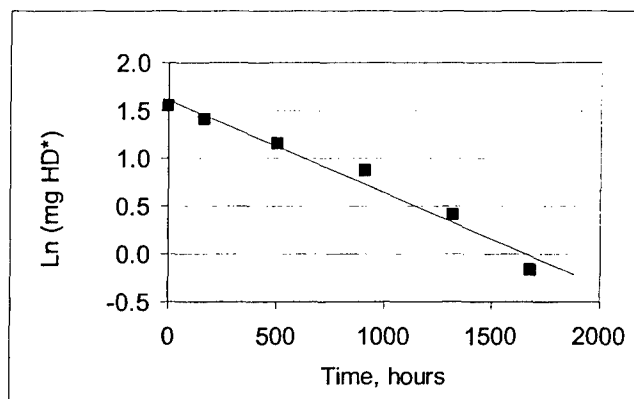
Figure 7. First-order kinetic plot for HD* loss on ambient concrete C03.

3.3 Aged Concrete with Added Water.

The initial spectrum of the CEPS* on wet, aged concrete (C90) showed fewer spinning side bands than the ambient sample; these accounted for 20% of the total integrated peak area and were less obvious than on the dry sample since the use of a faster spin rate moved the spinning side bands out of the area of observation. At 9 months, 50% of the CEPS* had converted to the ether and the alcohol, at 70 and 61 ppm respectively. The sample was then

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heated to 50 °C; at the end of 6 weeks, there had been total conversion to products, and there were a total of five peaks present at 70, 64, 61, 37, and 34 ppm (Figure 8).

The initial spectrum of the HD* on wet concrete C90 showed fewer spinning side bands than on dry concrete, accounting for only 15% of the total integrated peak area, compared to 28% on the ambient concrete. The presence of fewer spinning side bands indicated a reduced interaction of the HD* with the substrate, likely due to the water displacing the sulfur mustard from the surface of the concrete. Multiple product peaks were seen in six days; the first-order half-life for HD* loss was 120 hr. After 11 days the changes in the chemical shifts were minimal. Because the product had chemical shifts similar to those of the mustard, it was difficult to detect the point at which all of the mustard had disappeared. Characteristic product chemical shifts observed were 70 ppm (ether), 65 ppm (sulfonium ion), 61 ppm (alcohol), 57 ppm (both sulfonium ions), and 27 ppm (H-2TG sulfonium ion); no elimination products were observed. Multiple species were observed at 30 to 45 ppm, but these chemical shifts were not diagnostic because they are present in many sulfur mustard degradation products. Over the period of a year, the 27 ppm peak for the H-2TG disappeared and the 57 and 42 ppm H-2TG peaks decreased. The alcohol at 61 ppm grew slightly larger, thus indicating that the H-2TG was converting into TDG.

Figure 8. ^{13}C SSMAS NMR spectra of CEPS* and water on concrete C90; spectra in order from bottom to top were acquired at 1 hr, 9 months, and the 9-month sample at 50 °C for 6 weeks.
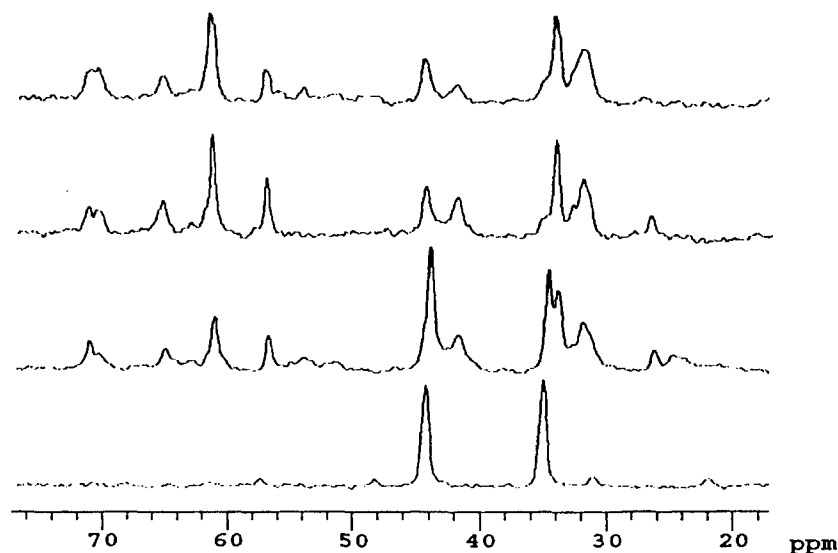
Figure 9. ^{13}C SSMAS NMR spectra of HD* and water on concrete C90; spectra in order from bottom to top were acquired at 1 hr (shown at 1/4 magnification), 6 days, 11 days, and 62 weeks.

3.4   Year-old Concrete with Added Water.
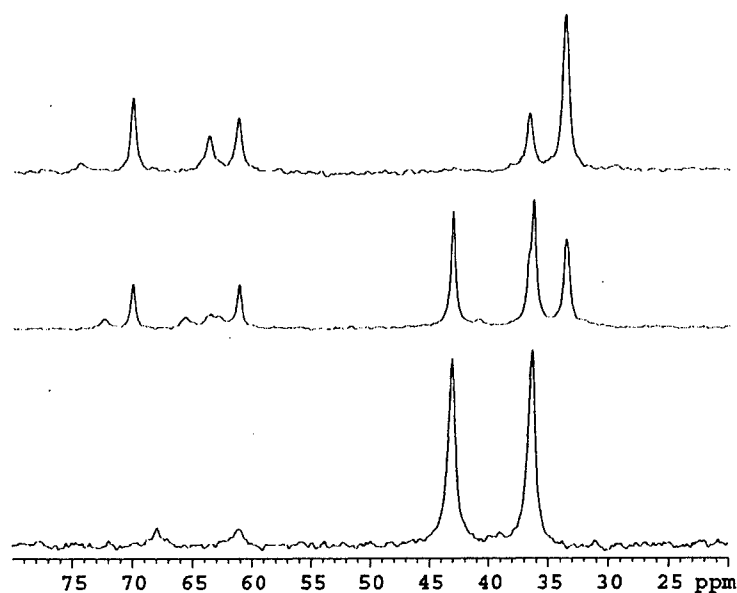
The products detected 9 months after CEPS* and water had been deposited onto concrete C03 were similar to those seen on the concrete C90, as was the time-scale over which the products were seen. No spinning side bands were seen in this sample, compared to 8% on the ambient concrete C03, thus indicating that the water had displaced the CEPS* from the surface of the concrete (Figure 10).

When HD* and water were placed on concrete C03 degradation products were seen at 6 days; HD* was still present at 11 days, yielding a calculated first-order half-life of 140 hr; no HD* was observed at 44 days. At 11 days, a large peak at 65 ppm, the sulfonium ion O(CH$_2$CH$_2$)$_2$S$^+$CH$_2$CH$_2$OH, was observed; the peak decreased during the following month. At 45 weeks, the major compounds present were TDG (61 and 33 ppm) and 1,4-oxathiane (71 and 32 ppm) with traces of vinyl species (132 and 111 ppm). There was an additional hydroxyl peak at 63 ppm. This may indicate an interaction of the TDG with the concrete, or the balance of a 2-hydroxyethyl vinyl (HOEVS) resonance (Figure 11).

To probe the reactions occurring on the concrete, after 62 weeks, 18 uL of neat, natural abundance 2-chloroethanol (63, 47 ppm), was added to the sample, which contained the products TDG and 1,4-oxathiane. After 24 hr the sulfonium ion O(CH$_2$CH$_2$)$_2$S$^+$CH$_2$CH$_2$OH was observed; over a period of two weeks it grew at the expense of the TDG and 1,4-oxathiane (Figure 12). The intensity of the 2-chloroethanol peaks remained unchanged.

Figure 10. ^{13}C SSMAS NMR spectra of CEPS* and water on concrete C03; spectra in order from bottom to top were acquired at 1 hr, 9 months, and the 9-month sample at 50 °C for 6 weeks.
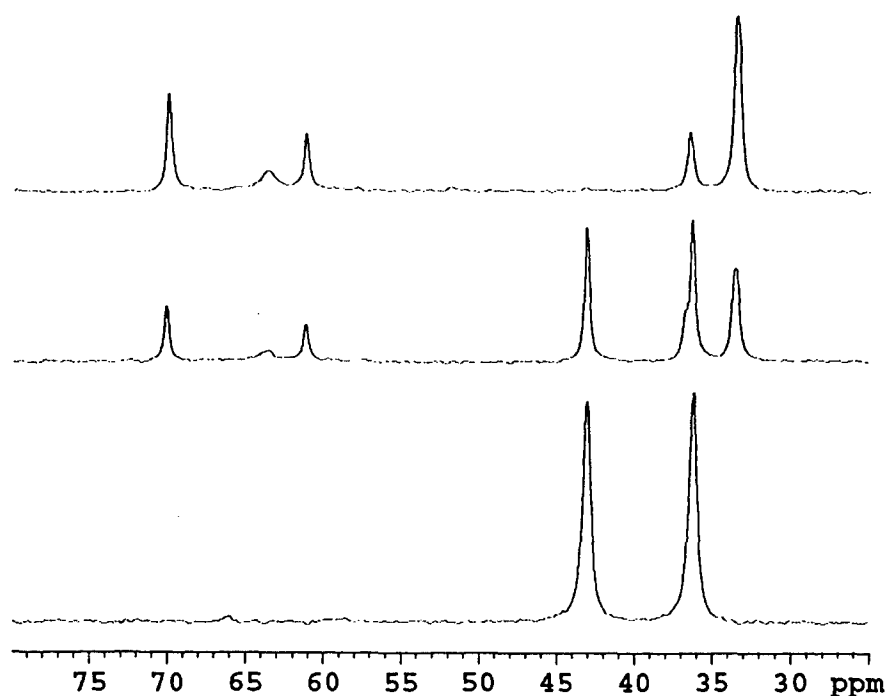
4.   DISCUSSION

The CEPS* barely degraded on the ambient C90 concrete over the period of 11 months, whereas the HD* absorbed into the ambient C90 concrete over a period of months, and had degraded to form the sulfonium ion by 11 months. By contrast, on the ambient C03 concrete, the HD* degraded with a 25-day half-life, and the CEPS* degraded with a 19-week half-life. The trend of faster reactivity for newer concrete samples was also observed in the degradation of VX on concrete.[29] For VX on concrete the use of a year-old concrete rather than an aged sample caused the reaction time to decrease from several months to 5 days; due to the pH of the concrete.[30] It was also observed for VX on aged concrete that there was an initial fast reaction, which corresponded to the reaction of one monolayer of VX followed by a slower, bulk reaction.[31] Assuming a molecular surface area[8] of 38 Å[30], 5 mg of HD*, the amount typically used in these experiments, would require 7 m^2 for monolayer coverage of the concrete. However, the available surface area was only 0.4 m^2/g, thus indicating that either the HD* degradation was a bulk phenomenon or that the HD* was able to migrate to any surface active sites, and that the products migrated away.

Figure 11. ^{13}C SSMAS NMR spectra of HD* and water on concrete C03: spectra from bottom to top were acquired at 1 hr, 6 days (shown at 1/5 magnification), 11 days, 44 days, 45 weeks and 62 weeks.
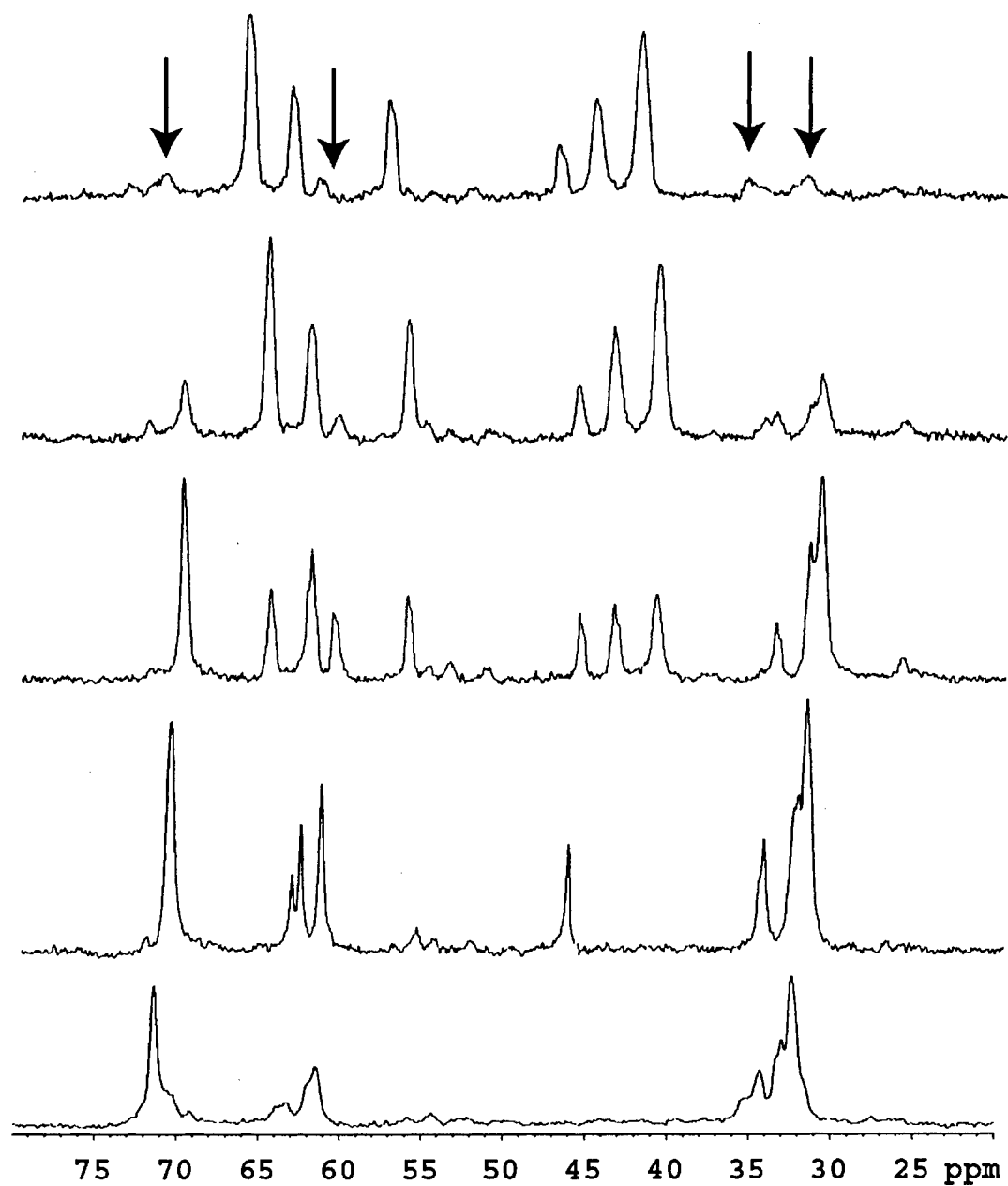
Figure 12. ^{13}C SSMAS NMR spectra of HD* and water on concrete C03; spectra from bottom to top are: 62-week HD* degradation products; degradation products plus 2-chloroethanol; one day after the addition of 2-chloroethanol; one week after the addition of 2-chloroethanol; and two weeks after the addition of 2-chloroethanol. The arrows show the loss of TDG and 1,4-oxathiane.

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The pH values and surface area of the concrete increased upon grinding. The prior VX on concrete studies measured VX half-lives of 28 days on crushed concrete and 96 days on monolithic concrete. Thus, grinding the concrete increased the decomposition rate by a factor of ~3. Similar experiments of sulfur mustard on ambient concrete monoliths of C03 showed a half-life loss of 17 days,[32] but no products were seen. The half-life for sulfur mustard decomposition on the crushed C03, 25 weeks, was only ~50% faster than on the monolith. Hence, degradation rates for VX and sulfur mustard were consistently faster on crushed concrete (which had more alkaline surface available to the agent) than on monoliths and were faster on newer, more alkaline concrete samples. The decrease in alkalinity of concrete as it ages is a known process, due to the gradual carbonation of the calcium oxide, forming calcium carbonate.[33]

In aqueous solution, CEPS* hydrolysis was 10.5 times slower than HD* hydrolysis,[34] whereas on concrete it was only 5.3 times slower. CEPS* on ambient C90 concrete yielded only the alcohol, whereas on ambient C03 concrete it primarily yielded the ether, with a trace of the alcohol. Thus, the alkalinity of the surface increased the rate of CEPS* hydrolysis and the formation of ether. CEPS* on aged and year-old concrete with water produced the alcohol, ether, and a third, as-yet unidentified product with chemical shifts at 64 and 36 ppm, which may be an alcohol in which the O interacted with the surface similar to that proposed for the AgY zeolites.[26] No elimination products were seen.

The addition of water to the HD* yielded similar products and degradation times on both the aged and year-old concrete samples, with the exception of vinyl formation, which was only seen on the year-old concrete. The elimination product, vinyl, was only seen on the newer, more alkaline concrete, both ambient and wet. This is consistent with the observation of elimination products for HD* on alkaline MgO[18] and Alumina.[19]

The half-lives observed for the hydrolysis of sulfur mustard on concrete were 1500 times longer than those observed in dilute solution; 100 hr compared to 4 min, respectively. The much slower hydrolysis rate on concrete compared to aqueous solution, plus the formation of elimination and sulfonium ion products, showed that once formed, the 1-(2-chloroethyl)thiiranium, $ClCH_2CH_2S^+(CH_2)_2,$ reacted preferentially with HD rather than with H_2O. This was not surprising, because HD was highly solvated in dilute aqueous solution, whereas on the concrete the amount of water was enough to moisten the surface, but no free liquid was observed. The narrower peak widths obtained upon the addition of water indicated that the water absorbed on the hydrophilic concrete surface, and the mustard formed droplets between the concrete particles.

This work shows the benefits and detriments of using a half-mustard simulant. They were similar in that HD* and CEPS* formed ether and alcohol products, but the HD* additionally formed vinyl species, as well as the sulfonium ions H-2TG and $O(CH_2CH_2)_2S^+CH_2CH_2OH$.

The mechanism for the formation of H-2TG (Scheme 1) showed that it proceeded via CH and two sulfonium ion intermediates, CH-TG and H-TG. None of these were detected, and thus must have reacted quickly.

The degradation of H-2TG formed 1,4-oxathiane and TDG (Figures 6, 11). The proposed mechanisms for TDG formation from H-2TG (Schemes 2 and 3) may be intermolecular or intramolecular; they cannot currently be distinguished. 1,4-oxathiane would form from the TDG via condensation and elimination of water.
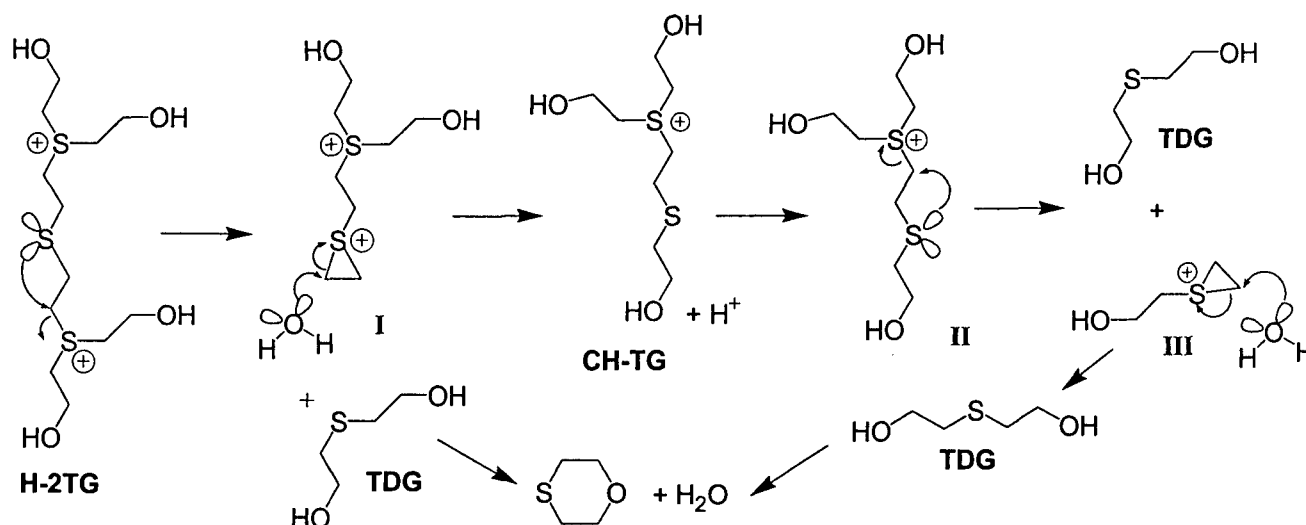
Scheme 2. Proposed mechanism for the intramolecular decomposition of H-2TG to TDG and 1,4-oxathiane.
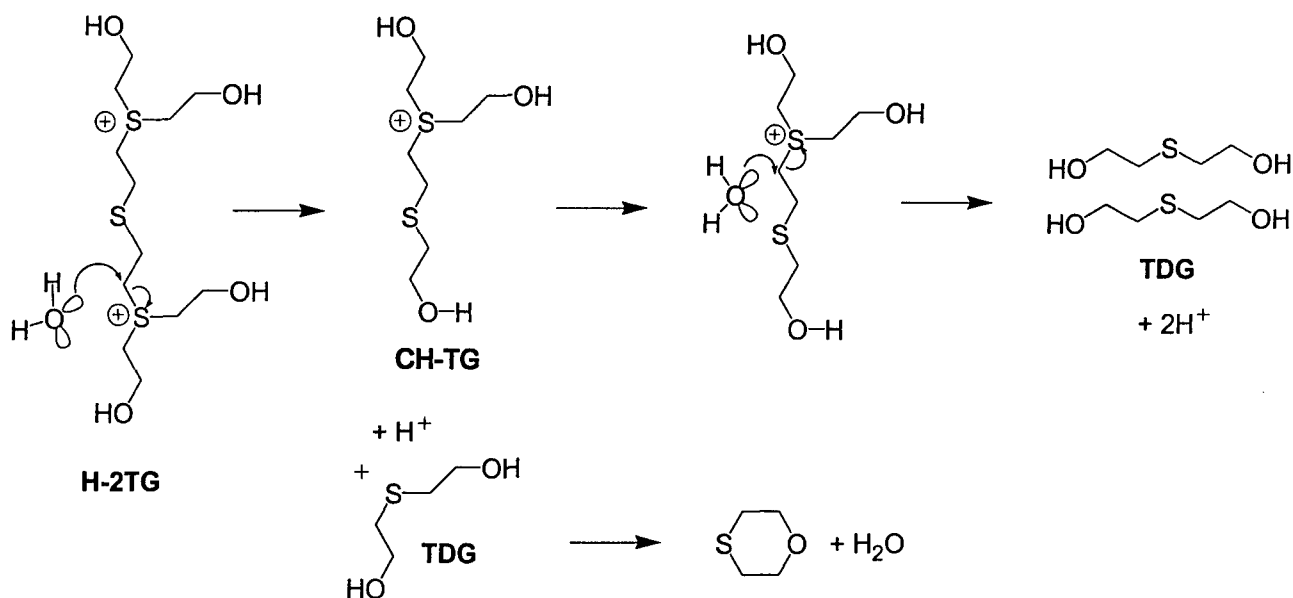
Scheme 3. Proposed mechanism for the intermolecular decomposition of H-2TG to TDG and 1,4-oxathiane.

The intermediates, CH-TG and H-TG, for H-2TG formation and decomposition, which were not detected in these spectra, are known to undergo an intermolecular decomposition

to form 1,4-dithiane and 2-chloroethanol (Scheme 4).[28] The 1,4-dithiane (29 ppm) was detected in some of the samples, as evidenced by a slightly higher integrated area for the 32 ppm peak than for the 71 ppm peak (Figures 6, 11). Stoichiometric amounts of 2-chloroethanol were not detected, which suggests the amount formed was small, and the resonances were hidden under other resonances.

According to Scheme 5, the sulfonium ion $O(CH_2CH_2)_2S^+CH_2CH_2OH$ (observed in Figures 6, 9, and 11) is formed from 2-chloroethanol and TDG,[28] and it decomposed to form 1,4-oxathiane and 2-chloroethanol. Thus, the net reaction was for the TDG to form 1,4-oxathiane with a 2-chloroethanol catalyst. The reaction between TDG and 2-chloroethanol was confirmed by adding 2-chloroethanol to a mixture of TDG and 1,4-oxathiane. The 1,4-oxathiane also reacted to form $O(CH_2CH_2)_2S^+CH_2CH_2OH$ (Figure 12).

The mass balance of the HD* on wet concrete samples and dry C03 was ~70%. Most of the initial total integrated peak area was lost in the first two days, coincident with the rapid growth of the 65 ppm peak; there was minimal loss thereafter. The apparent loss of integrated peak area may be due to low quantities of many intermediates that merged into the baseline. Mass balance was maintained for the CEPS samples.
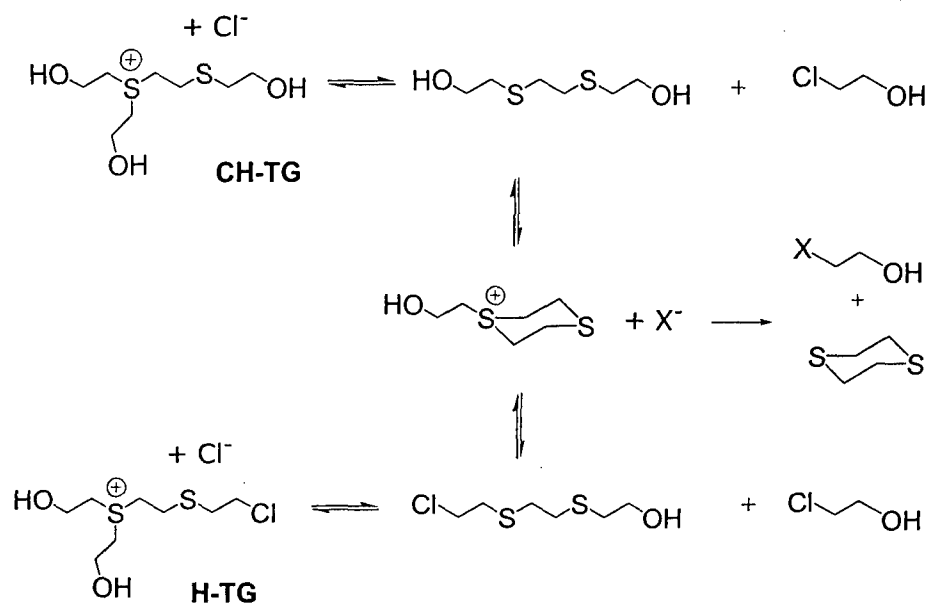
Scheme 4. Decomposition of CH-TG and H-TG
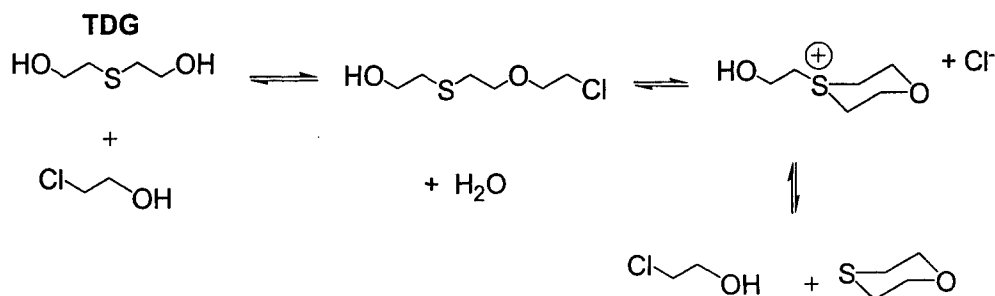
Scheme 5. Formation and decomposition of $O(CH_2CH_2)_2S^+CH_2CH_2OH$.

5. CONCLUSIONS

CEPS* degraded on all of the concrete samples to form the alcohol and ether. In 1 year, the degradation was complete only on the ambient year-old sample. The final products from sulfur mustard and CEPS* showed the presence of two species at the alcohol resonance, suggesting absorption of an alcohol onto the surface. Unlike sulfur mustard, CEPS* did not form any sulfonium ions, and in this respect, it was not a useful simulant for this system.

The major products of sulfur mustard degradation on concrete were non-toxic TDG and 1,4-oxathiane, with a trace of 1,4-dithiane. The degradation proceeded via the observed intermediates H-2TG and $O(CH_2CH_2)_2S^+CH_2CH_2OH$, and a multitude of intermediates that were not observed, including CH, CH-TG, H-TG and 2-chloroethanol. Vinyl species were a minor product formed only on the newer, alkaline concrete samples. The time period required for the formation of only non-toxic species was approximately 1 year on wet, year-old concrete, and more than a year on ambient year-old or aged concrete. Thus, sulfur mustard and its toxic degradation products may persist in concrete for months to years. The vapor and contact hazards of the products, as well as the mobility imparted to the products by rainfall, must be assessed by future studies.

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